# 1
# Basic Concepts

## 1.1
## Modelling Fundamentals

Models are an integral part of any kind of human activity. However, we are mostly unaware of this. Most models are qualitative in nature and are not formulated explicitly. Such models are not reproducible and cannot easily be verified or proven to be false. Models guide our activities, and throughout our entire life we are constantly modifying those models that affect our everyday behaviour. The most scientific and technically useful types of models are expressed in mathematical terms. This book focuses on the use of dynamic mathematical models in the field of chemical engineering.

### 1.1.1
### Chemical Engineering Modelling

The use of models in chemical engineering is well established, but the use of dynamic models, as opposed to the more traditional use of steady-state models for chemical plant analysis, is much more recent. This is reflected in the development of new powerful commercial software packages for dynamic simulation, which has arisen owing to the increasing pressure for design validation, process integrity and operation studies for which a dynamic simulator is an essential tool. Indeed it is possible to envisage dynamic simulation becoming a mandatory condition in the safety assessment of plant, with consideration of such factors as start up, shutdown, abnormal operation, and relief situations assuming an increasing importance. Dynamic simulation can thus be seen to be an essential part of any hazard or operability study, both in assessing the consequences of plant failure and in the mitigation of possible effects. Dynamic simulation is thus of equal importance in large scale continuous process operations, as in other inherently dynamic operations such as batch, semi-batch and cyclic manufacturing processes. Dynamic simulation also aids in a very positive sense in enabling a better understanding of process performance and is a powerful tool for plant optimisation, both at the operational and at the design stage. Furthermore steady-state operation is then seen in its rightful place as the end result of a dynamic process for which rates of change have become eventually zero.

The approach in this book is to concentrate on a simplified approach to dynamic modelling and simulation. Large scale commercial software packages for chemical engineering dynamic simulation are now very powerful and contain highly sophisticated mathematical procedures, which can solve both for the initial steady-state condition as well as for the following dynamic changes. They also contain extensive standard model libraries and the means of synthesising a complete process model by combining standard library models. Other important aspects are the provision for external data interfaces and built-in model identification and optimisation routines, together with access to a physical property data package. The complexity of the software, however, is such that the packages are often non-user friendly and the simplicity of the basic modelling approach can be lost in the detail of the solution procedures. The correct use of such design software requires a basic understanding of the sub-model blocks and hence of the methodology of modelling. Our simplified approach to dynamic modelling and simulation incorporates no large model library, no attached database and no relevant physical property package. Nevertheless quite realistic process phenomena can be demonstrated, using a very simple approach. Also, this can be very useful in clarifying preliminary ideas before going to the large scale commercial package, as we have found several times in our research. Again this follows our general philosophy of starting simple and building in complications as the work and as a full understanding of the process model progresses. This allows the use of models to be an explicit integral part of all our work.

Kapur (1988) has listed thirty-six characteristics or principles of mathematical modelling. Mostly a matter of common sense, it is very important to have them restated, as it is often very easy to lose sight of the principles during the active involvement of modelling. They can be summarised as follows:

1. The mathematical model can only be an approximation of real-life processes, which are often extremely complex and often only partially understood. Thus models are themselves neither good nor bad but should satisfy a previously well defined aim.
2. Modelling is a process of continuous development, in which it is generally advisable to start off with the simplest conceptual representation of the process and to build in more and more complexities, as the model develops. Starting off with the process in its most complex form often leads to confusion.
3. Modelling is an art but also a very important learning process. In addition to a mastery of the relevant theory, considerable insight into the actual functioning of the process is required. One of the most important factors in modelling is to understand the basic cause and effect sequence of individual processes.
4. Models must be both realistic and robust. A model predicting effects, which are quite contrary to common sense or to normal experience, is unlikely to be met with confidence.

## 1.1.2
## General Aspects of the Modelling Approach

An essential stage in the development of any model is the formulation of the appropriate mass and energy balance equations. To these must be added appropriate kinetic equations for rates of chemical reaction, rates of heat and mass transfer and equations representing system property changes, phase equilibrium, and applied control. The combination of these relationships provides a basis for the quantitative description of the process and comprises the basic mathematical model. The resulting model can range from a simple case of relatively few equations to models of great complexity. The greater the complexity of the model, however, the greater is then the difficulty in identifying the increased number of parameter values. One of the skills of modelling is thus to derive the simplest possible model, capable of a realistic representation of the process.

The application of a combined modelling and simulation approach leads to the following advantages:
1. Modelling improves understanding.
2. Models help in experimental design.
3. Models may be used predictively for design and control.
4. Models may be used in training and education.
5. Models may be used for process optimisation.

## 1.1.3
## General Modelling Procedure

One of the more important features of modelling is the frequent need to reassess both the basic theory (physical model), and the mathematical equations, representing the physical model (mathematical model), in order to achieve agreement, between the model prediction and actual process behaviour (experimental data).

As shown in Fig. 1.1, the following stages in the modelling procedure can be identified:
(1) The first involves the proper definition of the problem and hence the goals and objectives of the study.
(2) All the available knowledge concerning the understanding of the problem must be assessed in combination with any practical experience, and perhaps alternative physical models may need to be developed and examined.
(3) The problem description must then be formulated in mathematical terms and the mathematical model solved by computer simulation.
(4) The validity of the computer prediction must be checked. After agreeing sufficiently well with available knowledge, experiments must then be designed to further check its validity and to estimate parameter values. Steps (1) to (4) will often need to be revised at frequent intervals.
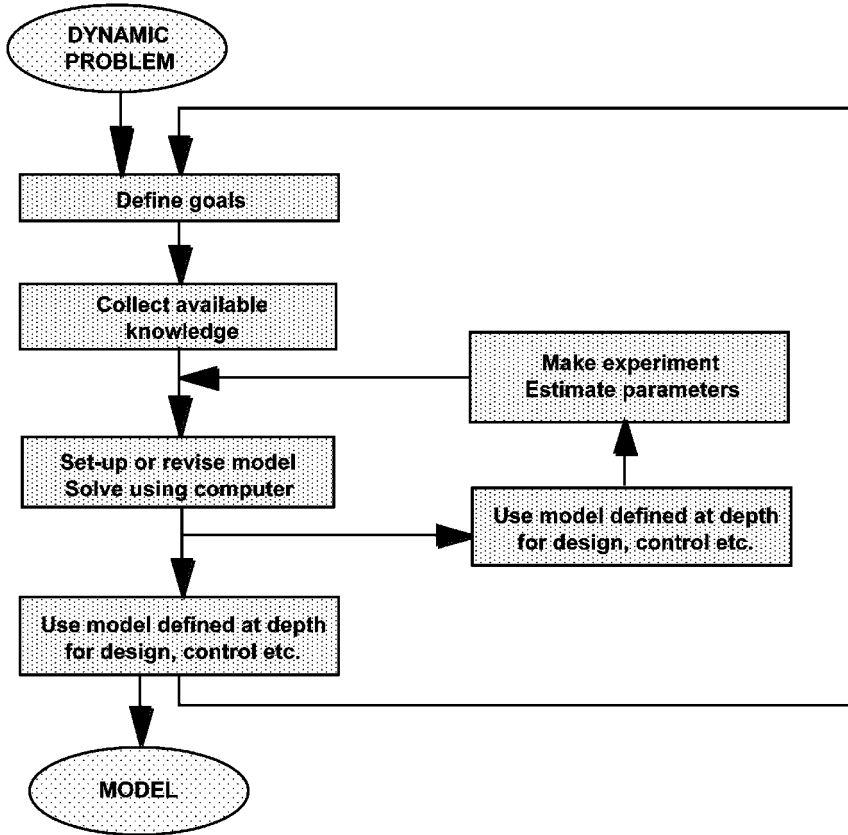(5) The model may now be used at the defined depth of development for design, control and for other purposes.

**Fig. 1.1** Steps in model building.

## 1.2
## Formulation of Dynamic Models

### 1.2.1
### Material Balance Equations

**Steady-State Balances**

One of the basic principles of modelling is that of the conservation of mass or matter. For a steady-state flow process, this can be expressed by the statement:

$$\begin{pmatrix} \text{Rate of mass flow} \\ \text{into the system} \end{pmatrix} = \begin{pmatrix} \text{Rate of mass flow} \\ \text{out of the system} \end{pmatrix}$$

**Dynamic Total Material Balances**

Most real situations are, however, such that conditions change with respect to time. Under these circumstances, a steady-state material balance is inappropriate and must be replaced by a dynamic or unsteady-state material balance, expressed as

$$\begin{pmatrix} \text{Rate of accumulation of} \\ \text{mass in the system} \end{pmatrix} = \begin{pmatrix} \text{Rate of} \\ \text{mass flow in} \end{pmatrix} - \begin{pmatrix} \text{Rate of} \\ \text{mass flow out} \end{pmatrix}$$

Here the rate of accumulation term represents the rate of change in the total mass of the system, with respect to time, and at steady state, this is equal to zero. Thus, the steady-state material balance is seen to be a simplification of the more general dynamic balance.

At steady state

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation of mass} \end{pmatrix} = 0 = (\text{Mass flow in}) - (\text{Mass flow out})$$

hence, when steady state is reached

$$(\text{Mass flow in}) = (\text{Mass flow out})$$

**Component Balances**

The previous discussion has been in terms of the total mass of the system, but most process streams, encountered in practice, contain more than one chemical species. Provided no chemical change occurs, the generalised dynamic equation for the conservation of mass can also be applied to each chemical component of the system. Thus for any particular component

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation of mass} \\ \text{of component} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow of} \\ \text{the component} \\ \text{into the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow of} \\ \text{the component out} \\ \text{of the system} \end{pmatrix}$$

**Component Balances with Reaction**

Where a chemical reaction occurs, the change, due to reaction, can be taken into account by the addition of a reaction rate term into the component balance equation. Thus in the case of material produced by the reaction

$$
\begin{pmatrix}
\text{Rate of} \\
\text{accumulation} \\
\text{of mass} \\
\text{of component} \\
\text{in the system}
\end{pmatrix}
=
\begin{pmatrix}
\text{Mass flow} \\
\text{of the} \\
\text{component} \\
\text{into} \\
\text{the system}
\end{pmatrix}
-
\begin{pmatrix}
\text{Mass flow} \\
\text{of the} \\
\text{component} \\
\text{out of} \\
\text{the system}
\end{pmatrix}
+
\begin{pmatrix}
\textbf{Rate of} \\
\textbf{production} \\
\textbf{of the} \\
\textbf{component} \\
\textbf{by the reaction}
\end{pmatrix}
$$

The principle of the component material balance can also be extended to the atomic level and can also be applied to particular elements.

Thus for the case of carbon, in say a fuel combustion process

$$
\begin{pmatrix}
\text{Rate of} \\
\text{accumulation} \\
\text{of carbon mass} \\
\text{in the system}
\end{pmatrix}
=
\begin{pmatrix}
\text{Mass flow} \\
\text{rate of} \\
\text{carbon into} \\
\text{the system}
\end{pmatrix}
-
\begin{pmatrix}
\text{Mass flow} \\
\text{rate of} \\
\text{carbon out} \\
\text{of the system}
\end{pmatrix}
$$

Note that the elemental balances do not involve additional reaction rate terms since the elements are unchanged by chemical reaction.

While the principle of the material balance is very simple, its application can often be quite difficult. It is important therefore to have a clear understanding of the nature of the system (physical model) which is to be modelled by the material balance equations and also of the methodology of modelling.

### 1.2.2
### Balancing Procedures

The methodology described below outlines five steps **I** through **V** to establish the model balances. The first task is to define the system by choosing the balance or control region. This is done using the following procedure:

### I. Choose the Balance Region Such That the Variables Are Constant or Change Little Within the System. Draw Boundaries Around the Balance Region

The balance region can vary substantially, depending upon the particular area of interest of the model, ranging from say the total reactor, a region of a reactor, a single phase within a reactor, to a single gas bubble or a droplet of liquid. The actual choice, however, will always be based on a region of assumed uniform composition, or on another property as in the case of population balances. Generally, the modelling exercises will involve some prior simplification of the real system. Often the system being modelled will be considered in terms of a representation, based on systems of tanks (stagewise or lumped parameter systems) or systems of tubes (differential systems), or even combinations of tanks and tubes.
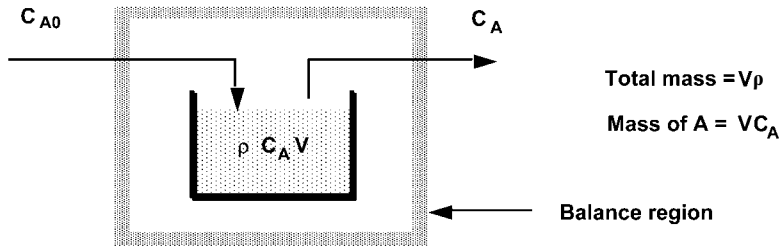
**Fig. 1.2** The balance region around the continuous reactor.

### 1.2.2.1 Case A: Continuous Stirred-Tank Reactor

If the tank is well-mixed, the concentrations and density of the tank contents are uniform throughout. This means that the outlet stream properties are identical with the tank properties, in this case concentration $C_A$ and density $\rho$. The balance region can therefore be taken around the whole tank (Fig. 1.2).

The total mass in the system is given by the product of the volume of the tank contents V (m$^3$) multiplied by the density $\rho$ (kg/m$^3$), thus V$\rho$ (kg). The mass of any component A in the tank is given in terms of actual mass or number of moles by the product of volume V times the concentration of A, $C_A$ (kg of A/m$^3$ or kmol of A/m$^3$), thus giving VC$_A$ in kg or kmol.

### 1.2.2.2 Case B: Tubular Reactor

In the case of tubular reactors, the concentrations of the products and reactants will vary continuously along the length of the reactor, even when the reactor is operating at steady state. This variation can be regarded as being equivalent to that of the time of passage of material as it flows along the reactor and is equivalent to the time available for reaction to occur. Under steady-state conditions the concentration at any position along the reactor will be constant with respect to time, though not with position. This type of behaviour, obtained with tubular reactors, can be approximated by choosing the incremental volume of
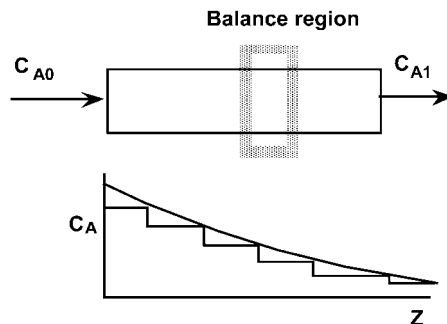


**Fig. 1.3** The tubular reactor concentration gradients.

**Lumped parameter**

Homogeneous (well-mixed) No
spatial variations

Concentration = f(time only)

Spatial variations

Concentration = f(time and position)

**Distributed parameter**
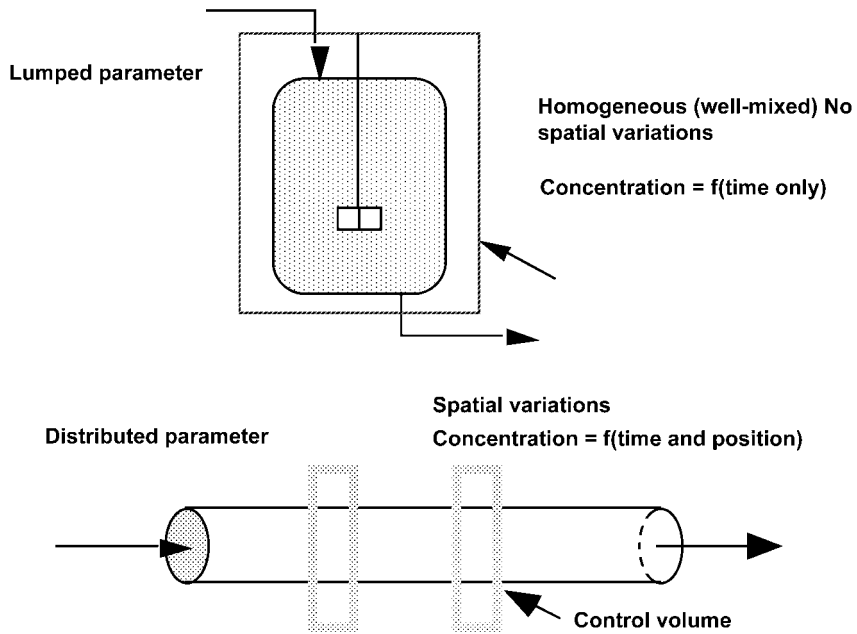
Control volume

**Fig. 1.4** Choosing balance regions for lumped and distributed parameter systems.

the balance regions sufficiently small so that the concentration of any component within the region can be assumed approximately uniform. Thus in this case, many uniform property sub-systems (well-stirred tanks or increments of different volume but all of uniform concentration) comprise the total reactor volume. This situation is illustrated in Fig. 1.3.

The basic concepts of the above lumped parameter and distributed parameter systems are shown in Fig. 1.4.

### 1.2.2.3 Case C: Coffee Percolator

A coffee percolator operates by circulating a stream of boiling coffee solution from the reservoir in the base of the coffee pot up through a central rise-pipe to the top of a bed of coffee granules, through which the solution then percolates, before returning in a more concentrated state to the base reservoir, as shown in Fig. 1.5.

The above system can be thought of as consisting of two parts with 1) the base reservoir acting effectively as a single well-stirred tank and 2) a fixed bed system of coffee granules irrigated by the flowing liquid stream. Solute coffee is removed from the granules by mass transfer under the action of a concentration driving force and is extracted into the liquid.

The concentrations of the coffee, both in the granules and in the liquid flowing through the bed, will vary continuously both with distance and with time. The behaviour of the packed bed is therefore best approximated by a series of
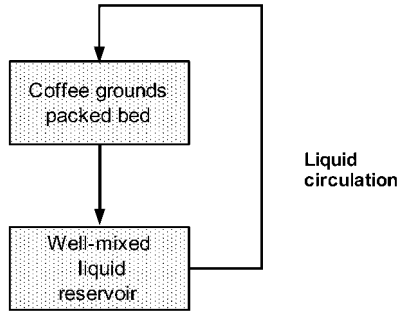
**Fig. 1.5** Conceptual of coffee percolator.

many uniform property subsystems. Each segment of solid is related to its appropriate segment of liquid by interfacial mass transfer, as shown in Fig. 1.6.

The resulting model would therefore consist of component balance equations for the soluble component written over each of the many solid and liquid subsystems of the packed bed, combined with the component balance equation for the coffee reservoir. The magnitude of the recirculating liquid flow will depend on the relative values of the pressure driving force generated by the boiling liquid and the fluid flow characteristics of the system.

The concept of modelling a coffee percolator as a dynamic process comes from a problem first suggested by Smith et al. (1970).
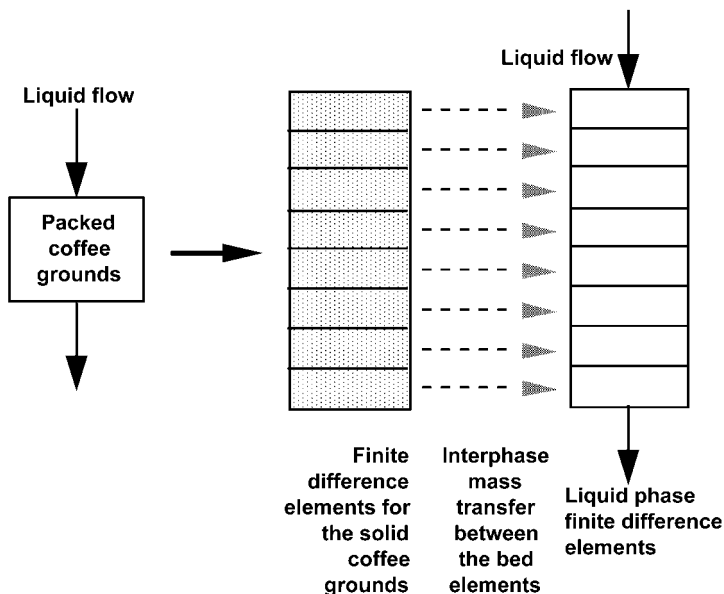


**Fig. 1.6** Modelling concepts for the packed bed solid-liquid extraction process of coffee percolation.
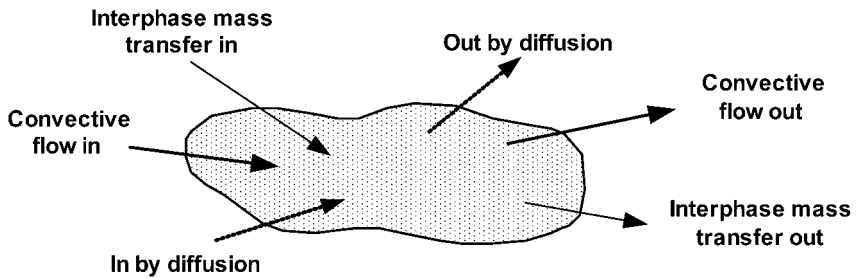
**Fig. 1.7** Balance region showing convective and diffusive flows as well as interphase mass transfer in and out.

### II. Identify the Transport Streams Which Flow Across the System Boundary

Having defined the balance regions, the next task is to identify all the relevant inputs and outputs to the system (Fig. 1.7). These may be well-defined physical flow rates (convective streams), diffusive fluxes, but may also include interphase transfer rates.

It is important to assume transfer to occur in a particular direction and to specify this by means of an arrow. This direction may reverse itself, but the change will be accommodated by a reversal in sign of the transfer rate term.

### III. Write the Material Balance in Word Form

This is an important step because it helps to ensure that the resulting mathematical equation will have an understandable physical meaning. Just starting off by writing down equations is often liable to lead to fundamental errors, at least on the part of the beginner. All balance equations have a basic logic, as expressed by the generalised statement of the component balance given below, and it is very important that the model equations also retain this. Thus

$$
\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{into} \\ \text{the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{out of} \\ \text{the system} \end{pmatrix} + \begin{pmatrix} \text{Rate of} \\ \text{production} \\ \text{of the} \\ \text{component by} \\ \text{the reaction} \end{pmatrix}
$$

This can be abbreviated as

$$
(\text{Accumulation}) = (\text{In}) - (\text{Out}) + (\text{Production})
$$

**IV. Express Each Balance Term in Mathematical Form with Measurable Variables**

**A. Rate of Accumulation Term**

This is given by the rate of change of the mass of the system, or the mass of some component within the system, with changing time and is expressed as the derivative of the mass with respect to time. Hence

$$\left( \begin{array}{l} \text{Rate of accumulation of mass} \\ \text{of component i within the system} \end{array} \right) = \left( \frac{dM_i}{dt} \right)$$

where M is in kg or mol and time is in h, min or s.

Volume, concentration and, in the case of gaseous systems, partial pressure are usually the measured variables. Thus for any component i

$$\frac{dM_i}{dt} = \frac{d(VC_i)}{dt}$$

where $C_i$ is the concentration of component i (kg/m$^3$). In the case of gases, the Ideal Gas Law can be used to relate concentration to partial pressure and mol fraction. Thus,

$$p_i V = n_i RT$$

where $p_i$ is the partial pressure of component i, within the gas phase system, and R is the Ideal Gas Constant, in units compatible with p, V, n and T.

In terms of concentration,

$$C_i = \frac{n_i}{V} = \frac{p_i}{RT} = \frac{y_i P}{RT}$$

where $y_i$ is the mol fraction of the component in the gas phase and P is the total pressure of the system.

The accumulation term for the gas phase can be therefore written in terms of number of moles as

$$\frac{dn_i}{dt} = \frac{d(VC_i)}{dt} = \frac{d\left( \frac{p_i V}{RT} \right)}{dt} = \frac{d\left( \frac{y_i PV}{RT} \right)}{dt}$$

For the total mass of the system

$$\frac{dM}{dt} = \frac{d(V\rho)}{dt}$$

with units

$$\frac{kg}{s} = \frac{kg}{m^3} \frac{m^3}{s}$$

## B. Convective Flow Terms

Total mass flow rates are given by the product of volumetric flow multiplied by density. Component mass flows are given by the product of volumetric flow rates multiplied by concentration.

$$(\text{Convective mass flow rate}) = (\text{Volumetric flow rate}) \left( \frac{\text{Mass}}{\text{Volume}} \right)$$

for the total mass flow

$$\dot{M} = \frac{dM}{dt} = F\rho$$

and for the component mass flow

$$\dot{M}_i = \frac{dM_i}{dt} = FC_i$$

with units

$$\frac{kg}{s} = \frac{m^3}{s} \frac{kg}{m^3}$$

A stream leaving a well-mixed region, such as a well-stirred tank, has the identical properties as in the system, since for perfect mixing the contents of the tank will have spatially uniform properties, which must then be identical to the properties of the fluid leaving at the outlet. Thus, the concentrations of component i both within the tank and in the tank effluent are the same and equal to $C_{i1}$, as shown in Fig. 1.8.
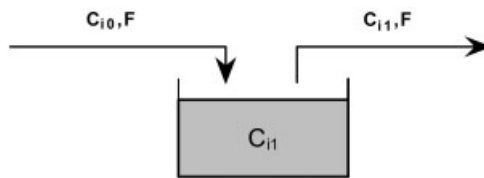


**Fig. 1.8** Convective flow terms for a well-mixed tank reactor.

## C. Diffusion of Components

As shown in Fig. 1.9, diffusional flow contributions in engineering situations are usually expressed by Fick's Law for molecular diffusion

$$j_i = -D_i \frac{dC_i}{dZ}$$

where $j_i$ is the flux of any component i flowing across an interface (kmol/m$^2$ s or kg/m$^2$ s) and $dC_i/dZ$ (kmol/m$^3$ m) is the concentration gradient and $D_i$ is the diffusion coefficient of component i (m$^2$/s) for the material.
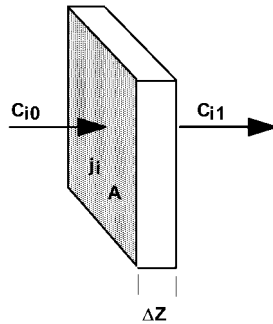


**Fig. 1.9** Diffusion flux $j_i$ driven by concentration gradient $(C_{i0}–C_{i1})/\Delta Z$ through surface area A.

In accordance with Fick's Law, diffusive flow always occurs in the direction of decreasing concentration and at a rate, which is proportional to the magnitude of the concentration gradient. Under true conditions of molecular diffusion, the constant of proportionality is equal to the molecular diffusivity of the component i in the system, $D_i$ (m$^2$/s). For other cases, such as diffusion in porous matrices and for turbulent diffusion applications, an effective diffusivity value is used, which must be determined experimentally.

The concentration gradient may have to be approximated in finite difference terms (finite differencing techniques are described in more detail in Sections 4.2 to 4.4). Calculating the mass diffusion rate requires knowledge of the area, through which the diffusive transfer occurs, since

$$\begin{pmatrix} \text{Mass rate} \\ \text{of} \\ \text{component i} \end{pmatrix} = - \begin{pmatrix} \text{Diffusivity} \\ \text{of} \\ \text{component i} \end{pmatrix} \begin{pmatrix} \text{Concentration} \\ \text{gradient} \\ \text{of i} \end{pmatrix} \begin{pmatrix} \text{Area} \\ \text{perpendicular} \\ \text{to transport} \end{pmatrix}$$

$$j_i A = -D_i \left( \frac{dC_i}{dZ} \right) A$$

The concentration gradient can often be approximated by difference quantities, where

$$j_i A = -D_i \left(\frac{\Delta C_i}{\Delta Z}\right) A$$

with units

$$\frac{kg}{s\,m^2} m^2 = \frac{m^2}{s}\,\frac{kg}{m^3}\,\frac{1}{m}\,m^2$$

### D. Interphase Transport

Interphase mass transport also represents a possible input to or output from the system. In Fig. 1.10, transfer of a soluble component takes place across the interface which separates the two phases. Shown here is the transfer from phase G to phase L, where the separate phases may be gas, liquid or solid.
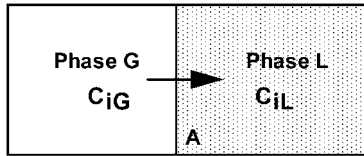


**Fig. 1.10** Transfer across an interface of area A from phase G to phase L.

When there is transfer from one phase to another, the component balance equations must consider this. Thus taking a balance for component i around the well-mixed phase G, with transfer of i from phase G to phase L, gives

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of i} \\ \text{in phase G} \end{pmatrix} = - \begin{pmatrix} \text{Rate of interfacial} \\ \text{mass transfer of i} \\ \text{from phase G} \\ \text{into phase L} \end{pmatrix}$$

This form of the transfer rate equation will be examined in more detail in Section 1.4. Suffice it to say here that the rate of transfer can be expressed in the form shown below

$$\begin{pmatrix} \text{Rate of} \\ \text{mass transfer} \end{pmatrix} = \begin{pmatrix} \text{Mass transfer} \\ \text{coefficient} \end{pmatrix} \begin{pmatrix} \text{Area of} \\ \text{the interface} \end{pmatrix} \begin{pmatrix} \text{Concentration} \\ \text{driving force} \end{pmatrix}$$

$$Q = KA\Delta C$$

The units of the transfer rate equation (with appropriate molar quantities) are

$$\frac{kmol}{s} = \frac{m}{s}\,m^2\,\frac{kmol}{m^3}$$

where Q is the total mass transfer rate, A is the total interfacial area for mass transfer ($m^2$), $\Delta C$ is the concentration driving force ($kmol/m^3$), and K is the overall mass transfer coefficient (m/s). It is important to note that the concentration driving force is represented as a difference between the actual concentration and the corresponding equilibrium value and is not a simple difference between actual phase concentrations. Mass transfer rates can be converted to mass flows (kg/s), by multiplying by the molar mass of the component.

### E. Production Rate

The production rate term allows for the production or consumption of material by chemical reaction and can be incorporated into the component balance equation. Thus,

$$
\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{into} \\ \text{the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow} \\ \text{of the} \\ \text{component} \\ \text{out of} \\ \text{the system} \end{pmatrix} + \begin{pmatrix} \textbf{Rate of} \\ \textbf{production} \\ \textbf{of the} \\ \textbf{component by} \\ \textbf{the reaction} \end{pmatrix}
$$

Chemical production rates are often expressed on a molar basis but can be easily converted to mass flow quantities (kg/s). The material balance equation can then be expressed as

$$
\begin{pmatrix} \text{Mass rate} \\ \text{of production} \\ \text{of component A} \end{pmatrix} = \begin{pmatrix} \text{Reaction} \\ \text{rate per} \\ \text{unit volume} \end{pmatrix} \begin{pmatrix} \text{Volume} \\ \text{of the} \\ \text{system} \end{pmatrix}
$$

$$
R_A = r_A V
$$

where $R_A$ is the total reaction rate. The units are

$$
\frac{kg}{s} = \frac{kg}{s\,m^3} m^3
$$

Equivalent molar quantities may also be used. The quantity $r_A$ is positive when A is formed as product, and $r_A$ is negative when reactant A is consumed.

### V. Introduce Other Relationships and Balances Such That the Number of Equations Equals the Number of Dependent Variables

The system material balance equations are often the most important elements of any modelling exercise, but are themselves rarely sufficient to completely for-

mulate the model. Thus other relationships are needed to complete the model in terms of other important aspects of behaviour in order to satisfy the mathematical rigour of the modelling, such that the number of unknown variables must be equal to the number of defining equations.

Examples of this type of relationships, which are not based on balances, but which nevertheless form a very important part of any model are:

- Reaction stoichiometry.
- Reaction rates as functions of concentration and temperature.
- Equations of state or Ideal Gas Law behaviour.
- Physical property correlations as functions of concentration, temperature, etc.
- Hydraulic flow equations.
- Pressure variations as a function of flow rate.
- Equilibrium relationships (e.g., Henry's law, relative volatilities, etc.).
- Activity coefficients.
- Dynamics of measurement instruments, as a function of instrument response time.
- Controller equations with an input variable dependent on a measured variable.
- Correlations for mass transfer coefficients, gas holdup volume, and interfacial area, as functions of system physical properties and agitation rate or flow velocity, etc.

How these and other relationships are incorporated within the development of particular modelling instances is illustrated, throughout the text and in the simulation examples.

### 1.2.3
### Total Material Balances

In this section, the application of the total material balance principle is presented. Consider some arbitrary balance region, as shown in Fig. 1.11 by the shaded area. Mass accumulates within the system at a rate $dM/dt$, owing to the competing effects of a convective flow input (mass flow rate in) and an output stream (mass flow rate out).
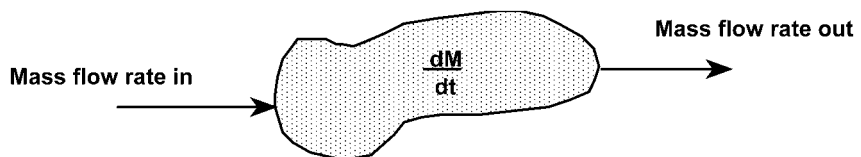


**Fig. 1.11** Balancing the total mass of an arbitrary system.

The total material balance is expressed by

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation of mass} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow} \\ \text{into the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow out} \\ \text{of the system} \end{pmatrix}$$

or in terms of volumetric flow rates F, densities $\rho$, and volume V,

$$\frac{dM}{dt} = \frac{d(\rho_1 V)}{dt} = F_0\rho_0 - F_1\rho_1$$

When densities are equal, as in the case of water flowing in and out of a tank

$$\frac{dV}{dt} = F_0 - F_1$$

The steady-state condition of constant volume in the tank (dV/dt=0) occurs when the volumetric flow in, $F_0$, is exactly balanced by the volumetric flow out, $F_1$. Total material balances therefore are mostly important for those modelling situations in which volumes are subject to change, as in simulation examples CONFLO, TANKBLD, TANKDIS and TANKHYD.

### 1.2.3.1  **Case A: Tank Drainage**
A tank of diameter D, containing liquid of depth H, discharges via a short base connection of diameter d, as shown in Fig. 1.12 (Brodkey and Hershey, 1988).

In this case, the problem involves a combination of the total material balance with a hydraulic relationship, representing the rate of drainage.
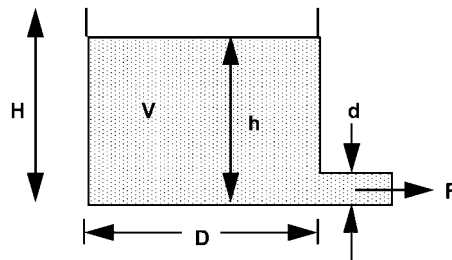


**Fig. 1.12** Liquid discharge from the bottom of a tank.

For zero flow of liquid into the tank and assuming constant density conditions, the total material balance equation becomes

$$\frac{dV}{dt} = -F$$

Assuming the absence of any frictional flow effects, the outlet flow velocity, v, is related to the instantaneous depth of liquid within the tank, by the relationship

$$v = (2gh)^{1/2}$$

where

$$F = \frac{\pi d^2}{4} v$$

and

$$V = \frac{\pi D^2}{4} h$$

v is the discharge pipe velocity, V is the volume of liquid in the tank, h is the depth of liquid in the tank and g is the constant of gravitational acceleration.

The above equations are then sufficient to define the model which has the following simple analytical solution

$$h = \left( \sqrt{H} - \frac{d^2}{D^2} \sqrt{\frac{g}{2}} t \right)^2$$

where H is the liquid depth at time t=0.

However, with a time variant flow of liquid into the tank, then analytical solution is not so simple. The problem is treated in more detail in simulation example TANKDIS.

### 1.2.4
### Component Balances

Each chemical species, in the system, can be described by means of a component balance around an arbitrary, well-mixed, balance region, as shown in Fig. 1.13.

In the case of chemical reaction, the balance equation is represented by

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component i} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow of} \\ \text{component i} \\ \text{into} \\ \text{the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow of} \\ \text{component i} \\ \text{out of} \\ \text{the system} \end{pmatrix} \begin{pmatrix} \text{Rate of} \\ \text{production of} \\ \text{component i} \\ \text{by reaction} \end{pmatrix}$$
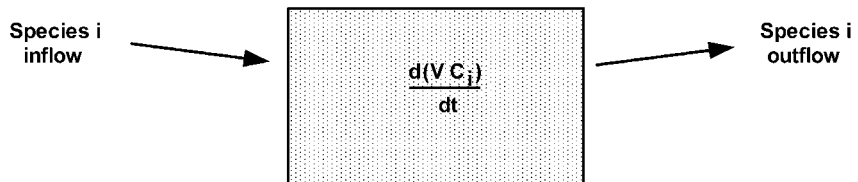


**Fig. 1.13** Component balancing for species i.

Expressed in terms of volume, volumetric flow rate and concentration, this is equivalent to

$$\frac{d(VC_i)}{dt} = (F_0 C_{i0}) - (F_1 C_{i1}) + (r_i V)$$

with dimensions of mass/time

$$\frac{m^3 \frac{kg}{m^3}}{s} = \frac{m^3}{s}\frac{kg}{m^3} - \frac{m^3}{s}\frac{kg}{m^3} + \frac{kg}{m^3 s}m^3 = \frac{kg}{s}$$

In the case of an input of component i to the system by interfacial mass transfer, the balance equation now becomes

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component i} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Mass flow of} \\ \text{component i} \\ \text{into} \\ \text{the system} \end{pmatrix} - \begin{pmatrix} \text{Mass flow of} \\ \text{component i} \\ \text{out of} \\ \text{the system} \end{pmatrix} + \begin{pmatrix} \text{Rate of} \\ \text{interfacial} \\ \text{transfer} \\ \text{of component i} \\ \text{into the system} \end{pmatrix}$$

$$\frac{d(VC_i)}{dt} = (F_0 C_{i0}) - (F_1 C_{i1}) + Q_i$$

where $Q_i$, the rate of mass transfer, is given by

$$Q_i = K_i A \Delta C_i$$

### 1.2.4.1 Case A: Waste Holding Tank

A plant discharges an aqueous effluent at a volumetric flow rate F. Periodically, the effluent is contaminated by an unstable noxious waste, which is known to decompose at a rate proportional to its concentration. The effluent must be diverted to a holding tank, of volume V, prior to final discharge, as in Fig. 1.14 (Bird et al. 1960).
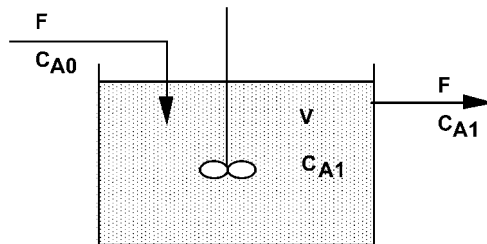


**Fig. 1.14** Waste holding tank.

This situation is one involving both a total and a component material balance, combined with a kinetic equation for the rate of decomposition of the waste component. Neglecting density effects, the total material balance equation is

$$\frac{dV}{dt} = F_0 - F_1$$

The rate of the decomposition reaction is given by

$$r_A = -kC_A$$

and the component balance equation by

$$\frac{d(VC_{A1})}{dt} = (F_0 C_{A0}) - (F_1 C_{A1}) + k_1 C_{A1} V$$

The tank starts empty, so that at time $t=0$, volume $V=0$, and the outlet flow from the tank $F_1=0$. At time $t=V/F_0$ the tank is full; then $F_1=F_0=F$, and the condition that $dV/dt=0$ also applies.

The above model equations can be solved analytically. For the conditions that, at time $t=0$, the initial tank concentration $C_A=0$, the tank is full and overflowing and that both $F$ and $C_{A0}$ are constant, analytical solution gives

$$C_A = C_{A0}(1 - Z)e^{(-Zt)} + Z$$

where

$$Z = \frac{F}{F + kV}$$

When the flow and inlet concentration vary with time, a solution is best obtained by numerical integration.

### 1.2.4.2 **Case B: Extraction from a Solid by a Solvent**

An agitated batch tank is used to dissolve a solid component from a solid matrix into a liquid solvent medium, as in Fig. 1.15.

For a batch system, with no inflow and no outflow, the total mass of the system remains constant. The solution to this problem thus involves a liquid-phase component material balance for the soluble material, combined with an expression for the rate of mass transfer of the solid into the liquid.

The component material balance is then

$$\begin{pmatrix} \text{Rate of accumulation} \\ \text{of the material} \\ \text{in the solvent} \end{pmatrix} = \begin{pmatrix} \text{Rate of transfer} \\ \text{of the solid} \\ \text{to the solvent} \end{pmatrix}$$
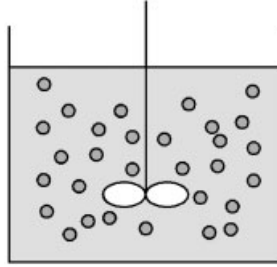
**Fig. 1.15** Agitated tank for dissolving solids.

giving

$$V_L \frac{dC_L}{dt} = k_L A(C_L^* - C_L)$$

where $V_L$ is the volume of the liquid, $C_L$ is the concentration of the component in the liquid, $k_L$ is the liquid phase mass transfer coefficient, A is the total interfacial area for mass transfer and $C_L^*$ is the equilibrium value.

The analytical solution to the above equation, assuming constant $V_L$, $k_L$, A and equilibrium concentration, $C_L^*$, is given by

$$\frac{C_L^* - C_L}{C_L^* - C_{L0}} = e^{-k_L At/V_L}$$

For the case, where the soluble component is leaching from an inert solid carrier, a separate solid phase component balance would be required to establish the solute concentration in the solid phase and hence the time-dependent value of the equilibrium concentration, $C_L^*$.

If during this extraction the volume and area of the solid remains approximately constant, the balance for the component in the solid phase is

$$V_S \frac{dC_S}{dt} = -k_L A(C_L^* - C_L)$$

where

$$C_L^* = f_{eq}(C_S)$$

and the subscript "eq" refers to the equilibrium condition.

1.2.5
**Energy Balancing**

Energy balances are needed whenever temperature changes are important, as caused by reaction heating effects or by cooling and heating for temperature control. For example, such a balance is needed when the heat of reaction causes a change in reactor temperature. This change obviously influences the reaction rate and therefore the rate of heat evolution. This is seen in the information flow diagram for a non-isothermal continuous reactor as shown in Fig. 1.16.

Energy balances are formulated by following the same set of guidelines as those given in Section 1.2.2 for material balances. Energy balances are however considerably more complex, because of the many different forms energy occurs in chemical systems. The treatment considered here is somewhat simplified, but is adequate to understand the non-isothermal simulation examples. The various texts cited in the reference section provide additional advanced reading in this subject.

Based on the law of conservation of energy, energy balances are a statement of the first law of thermodynamics. The internal energy depends not only on temperature, but also on the mass of the system and its composition. For that reason, material balances are almost always a necessary part of energy balancing.
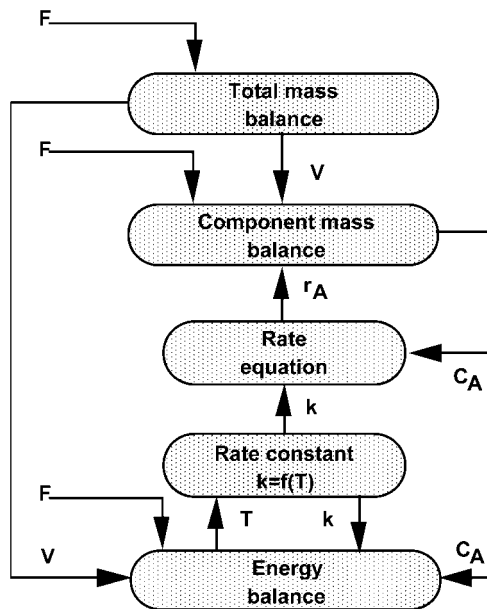


**Fig. 1.16** Information flow diagram for modelling a non-isothermal, chemical reactor, with simultaneous mass and energy balances.

For an open system with energy exchange across its boundaries, as shown in Fig. 1.17, the energy balance can be written as

$$
\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of energy} \end{pmatrix} = \begin{pmatrix} \text{Rate of} \\ \text{energy} \\ \text{input due} \\ \text{to flow} \end{pmatrix} - \begin{pmatrix} \text{Rate of} \\ \text{energy} \\ \text{output due} \\ \text{to flow} \end{pmatrix} + \begin{pmatrix} \text{Rate of} \\ \text{energy} \\ \text{input due} \\ \text{to transfer} \end{pmatrix}
$$

$$
- \begin{pmatrix} \text{Rate of work} \\ \text{done by the} \\ \text{system on the} \\ \text{surroundings} \end{pmatrix}
$$

$$
\frac{dE}{dt} = \sum_{i=1}^{S} N_{i0} E_{i0} - \sum_{i=1}^{S} N_{i1} E_{i1} + Q - W
$$

Here, E is the total energy of the system, $E_i$ is the energy per mole of component i, $N_i$ is the molar flow rate of component i, Q is the rate of energy input to the system due transfer and S is the total number of components (reactants and inerts).

The work term can be separated into flow work and other work $W_S$, according to

$$
W = - \sum_{i=1}^{S} N_{i0} P V_{i0} + \sum_{i=1}^{S} N_{i1} P V_{i1} + W_S
$$

$V_i$ is the molar volume of component i. The energy $E_i$ is the sum of the internal energy $U_i$, the kinetic energy, the potential energy and any other forms of energy. Of these various forms of energy, changes of internal energy are usually dominant in chemical systems. The other terms are usually neglected.

Internal energy, U, can be expressed in terms of enthalpy, H
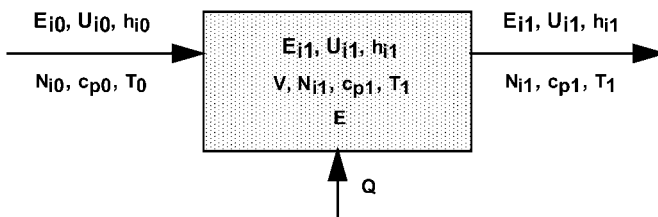
$$
E = U = H - (PV)
$$



**Fig. 1.17** A continuous reactor showing only the energy-related variables.

The accumulation term is given only in terms of enthalpies, since the $d(PV)$ term is usually negligible in chemical reactors.

$$\frac{dE}{dt} = \frac{d}{dt} \sum_{i=1}^{S} n_i h_{i1}$$

$h_i$ is the partial molar enthalpy of component i. Combining these equations and assuming the other work $W_S = 0$, yields the energy balance equation

$$\frac{d}{dt} \sum_{i=1}^{S} n_i h_{i1} = \sum_{i=1}^{S} N_{i0} h_{i0} - \sum_{i=1}^{S} N_{i1} h_{i1} + Q$$

Here, $n_i$ the number of moles of component i, $h_i$ the partial molar enthalpy and Q is the rate of energy input from the environment. Enthalpies are generally dependent on temperature where:

$$h_i = h_{i0} + \int_{T_0}^{T} c_{pi} dT$$

The temperature dependency for heat capacity can usually be described by a polynomial expression, e.g.,

$$c_p = a + bT + cT^2$$

where a, b and c are empirical constants.

A detailed derivation of the energy balance is given in various textbooks (e.g., Aris, 1989 and Fogler, 2005).

With $\frac{\partial h_{i1}}{\partial T} = c_{pi1}$ and $n_{i1} \sum \frac{\partial h_{i1}}{\partial n_k} = 0$, the accumulation term in the energy balance equation can be rewritten as

$$\frac{d}{dt} \sum_{i=1}^{S} n_i h_{i1} = \sum_{i=1}^{S} h_{i1} \frac{dn_{i1}}{dt} + \frac{dT_1}{dt} \sum_{i=1}^{S} n_{i1} c_{pi1}$$

For the solution of the energy balance it is necessary that this is combined with material balance relationships.

Using a general material balance for component i

$$\frac{dn_{i1}}{dt} = N_{i0} - N_{i1} + r_i V$$

multiplying this equation by $h_{i1}$ and summing for all the S components gives

$$\sum_{i=1}^{S} h_{i1} \frac{dn_{i1}}{dt} = \sum_{i=1}^{S} h_{i1} N_{i0} - \sum_{i=1}^{S} h_{i1} N_{i1} + V \sum_{i=1}^{S} r_i h_{i1}$$

Introducing the reaction enthalpy $\Delta H$

$$\sum_{i=1}^{S} r_i h_{i1} = \sum_{j=1}^{R} \frac{r_{ij}}{v_{ij}} (-\Delta H_j(T_1))$$

and allowing for R reactions to occur gives the general energy balance as:

$$\sum_{i=1}^{S} (n_{i1} c_{pi1}) \frac{dT_1}{dt} = \sum_{i=1}^{S} N_{i0} (h_{i0} - h_{i1}) + \sum_{j=1}^{R} \frac{r_{ij}}{v_{ij}} (-\Delta H_j(T_1)) + Q$$

where $c_{pi}$ is the partial molar heat capacity of component i, $R_{ij}$ the reaction rate of component i in reaction j, $v_{ij}$ the stoichiometric coefficient of component i in reaction j and $\Delta H_j(T_1)$ is the reaction enthalpy of reaction j at temperature $T_1$.

The heat of reaction $\Delta H$ is defined by

$$\Delta H = \sum_{i=1}^{n} v_i h_i \approx \sum_{i=1}^{n} v_i \Delta H_{Fi}$$

where $\Delta H_{Fi}$ is the heat of formation of component i.

Considering the above temperature dependencies, the complete heat balance can then be written in the following form

$$\sum_{i=1}^{S} (n_{i1} c_{pi1}) \frac{dT_1}{dt} = -\sum_{i=0}^{S} N_{i0} \int_{T_0}^{T_1} c_{pi} dT_1 + \sum_{j=1}^{R} \frac{r_{ij}}{v_{ij}} (-\Delta H_j(T_1)) + Q$$

This equation can be used directly for any well-mixed, batch, semi-batch or continuous volume element. The term on the left-hand side represents the rate of energy accumulation. The first term on the right-hand side depicts the energy needed to raise the temperature of the incoming reactants, including inert material, to the reactor temperature. The second term describes the heat released by the chemical reactions. Since $\Delta H$ is a function of state, the energy balance could also be formulated such that the reaction is considered to take place at the inlet temperature $T_0$, followed by heating the reactor contents to temperature $T_1$. The above general energy balance equation is applied in simulation example REVTEMP and in Case C (Section 1.2.5.3).

The general heat balance can often be simplified for special situations.

**Accumulation Term**

At moderate temperature changes, $c_{pi}$ may be assumed to be independent of temperature and therefore

$$\sum_{i=1}^{S} n_{i1} c_{pi1} \approx V \rho c_p$$

The total heat capacity in the accumulation term must also include the reactor parts. $c_p$ is the heat capacity per unit mass (J/kgk). Then

$$\sum_{i=1}^{S} n_{i1} c_{pi1} \frac{dT}{dt} \approx V \rho c_p \frac{dT}{dt}$$

with units

$$\text{mol} \frac{J}{\text{mol K}} \frac{K}{s} = m^3 \frac{kg}{m^3} \frac{J}{kg\, K} \frac{K}{s} = \frac{J}{s}$$

Thus the accumulation term has the units of (energy)/(time), for example J/s.

**Flow Term**

At moderate temperature changes $c_{pi}$ is again assumed constant and therefore the flow term is

$$- \sum_{i=0}^{S} N_{i0} \int_{T_0}^{T_1} c_{pi} dT_1 \approx F_0 \rho c_p (T_0 - T_1)$$

with the units

$$\frac{\text{mol}}{s} \frac{J}{\text{mol K}} K = \frac{m^3}{s} \frac{kg}{m^3} \frac{J}{kg\, K} K = \frac{J}{s}$$

This term actually describes the heating of the stream entering the system with temperature $T_0$ to the reaction temperature $T_1$, and is therefore only needed if streams are entering the system.

**Heat Transfer Term**

The important quantities in this term are the heat transfer area A, the temperature driving force or difference $(T_a - T_1)$, where $T_a$ is the temperature of the heating or cooling source, and the overall heat transfer coefficient U. The heat transfer coefficient, U, has units of (energy)/(time)(area)(degree), e.g., J/s $m^2$ K.

$$(\text{heat transfer rate}) = UA(T_a - T_1)$$

The units for $U A \Delta T$ are thus

$$\frac{J}{s} = \frac{J}{m^2 s K} m^2 K$$

The sign of the temperature difference determines the direction of heat flow. Here if $T_a > T_1$, heat flows into the reactor.

**Reaction Heat Term**

For exothermic reactions, the value of $\Delta H$ is by convention negative and for endothermic reactions positive. For a set of R individual reactions, the total rate of heat production by reaction is given by

$$r_Q V = \sum_{j=1}^{R} \frac{r_{ij}}{\nu_{ij}} (-\Delta H_j)$$

with the units

$$\frac{J}{m^3 s} m^3 = \frac{mol}{s} \frac{J}{mol} = \frac{J}{s}$$

**Other Heat Terms**

The heat of agitation may be important, depending on the relative magnitudes of the other heat terms in the general balance equation and especially with regard to highly viscous reaction mixtures. Other terms, such as heat losses from the reactor, by radiation or by mixing, can also be important in the overall energy balance equation.

**Simplified Energy Balance**

If specific heat capacities can be assumed constant and for zero mechanical work done to the system, the energy balance equation simplifies to

$$V \rho c_p \frac{dT_1}{dt} = F_0 \rho c_p (T_0 - T_1) + V r_Q + UA(T_a - T_1)$$

where the units of each term of the balance equation are energy per unit time (kJ/s). This equation can be applied to batch, semi-batch and continuous reactors. Most of the non-isothermal simulation examples in Chapter 5 use the above form of the energy balance.

### 1.2.5.1  **Case A: Continuous Heating in an Agitated Tank**

Liquid is fed continuously to a stirred tank, which is heated by internal steam coils (Fig. 1.18). The tank operates at constant volume conditions. The system is
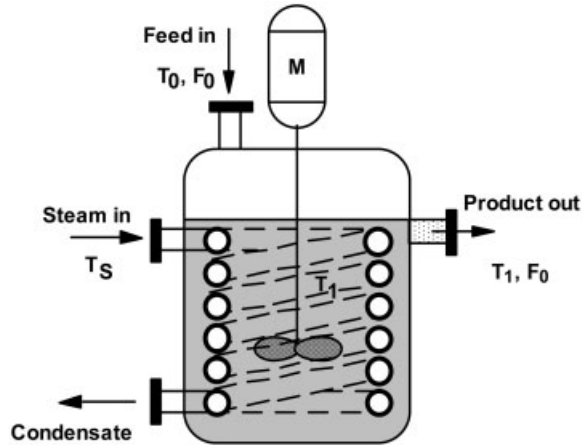
Fig. 1.18 Continuous stirred tank heated by internal steam coil.

therefore modelled by means of a dynamic heat balance equation, combined with an expression for the rate of heat transfer from the coils to the tank liquid.

With no heat of reaction and neglecting any heat input from the agitator, the heat balance equation becomes

$$V\rho c_p \frac{dT_1}{dt} = F_0 \rho c_p (T_0 - T_1) + UA(T_S - T_1)$$

where $T_S$ is the steam temperature.

### 1.2.5.2 Case B: Heating in a Filling Tank

The situation is the same as in Fig. 1.18 but without material leaving the reactor. Liquid flows continuously into an initially empty tank, containing a full-depth heating coil. As the tank fills, an increasing proportion of the coil is covered by liquid. Once the tank is full, the liquid starts to overflow, but heating is maintained. A total material balance is required to model the changing liquid volume and this is combined with a dynamic heat balance equation.

Assuming constant density, the material balance equation is

$$\frac{dV}{dt} = F_0 - F_1$$

where for time t less than the filling time, $V/F_0$, the outlet flow, $F_1$, equals zero, and for time t greater than $V/F_0$, $F_1$ equals $F_0$.

The heat balance is expressed by

$$V\rho c_p \frac{dT}{dt} = F_0 \rho c_p (T_0 - T) + UA(T_S - T)$$

Assuming $A_0$ is the total heating surface in the full tank, with volume $V_0$, and assuming a linear variation in heating area with respect to liquid depth, the heat transfer area may vary according to the simple relationship

$$A = A_0 \frac{V}{V_0}$$

More complex relationships can of course be derived, depending on the particular tank geometry concerned.

### 1.2.5.3 Case C: Parallel Reaction in a Semi-Continuous Reactor with Large Temperature Changes

Let us assume an adiabatic, semi-continuous reactor (see Section 3.2.4) with negligible input of mechanical energy (Fig. 1.19).

Two reactions are assumed to occur in parallel

$$A + B \rightarrow C$$

$$A + 2B \rightarrow D$$
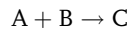
The total energy balance from Section 1.2.5 is given by

$$\sum_{i=1}^{S} (n_i c_{pi}) \frac{dT}{dt} = F_0 \sum_{i=1}^{S} C_{i0} \int_{T}^{T_0} c_{pi} dT + V \sum_{j=1}^{R} \frac{r_{ij}}{v_{ij}} (-\Delta H_j)$$

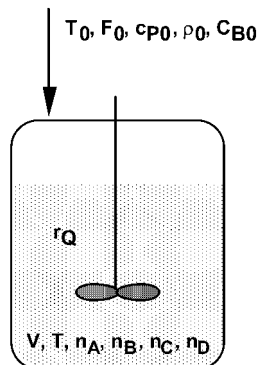In this case the number of components, S=4 and the number of reactions, R=2.



**Fig. 1.19** Adiabatic, semi-batch reactor.

The reaction enthalpies at standard temperature, $T_{St}$, are then

$$\Delta H_{1St} = \Delta H_{FC} - \Delta H_{FA} - \Delta H_{FB}$$

$$\Delta H_{2St} = \Delta H_{FD} - \Delta H_{FA} - 2\Delta H_{FB}$$

All heats of formation, $\Delta H_{Fi}$, are at standard temperature.

Assuming that the temperature dependencies for the specific heats are given by

$$c_{pi} = a_i + b_i T$$

then

$$h_i = h_{iSt} + \int_{T_{St}}^{T} c_{pi} dT = h_{iSt} + a_i(T - T_{St}) + \frac{b_i}{2}(T^2 - T_{St}^2)$$

and the reaction enthalpies, $\Delta H_1$ and $\Delta H_2$, at temperature T are

$$\Delta H_1 = \Delta H_{1St} + (a_C - a_A - a_B)(T - T_{St}) + \frac{b_C - b_A - b_B}{2}(T^2 - T_{St}^2)$$

$$\Delta H_2 = \Delta H_{2St} + (a_C - a_A - 2a_B)(T - T_{St}) + \frac{b_C - b_A - 2b_B}{2}(T^2 - T_{St}^2)$$

With stoichiometric coefficients, $\nu_{A1} = -1$ and $\nu_{A2} = -1$, the total heat of reaction is then

$$r_Q = \sum_{j=1}^{R} \frac{r_{ij}}{\nu_{ij}}(-\Delta H_j) = r_{A1}\,\Delta H_1 + r_{A2}\,\Delta H_2$$

The total heat capacity in the accumulation term is

$$V\rho c_p = \sum_{i=1}^{S}(n_i c_{pi}) = n_A(a_A + b_A T) + n_B(a_B + b_B T)$$
$$+ n_C(a_C + b_C T) + n_D(a_D + b_D T)$$

With only component B in the feed, the flow term in the energy balance becomes

$$F_0 \sum_{i=1}^{S} C_{i0} \int_{T}^{T_0} c_{pi} dT = F_0 C_{B0}\left[a_B(T_0 - T) + \frac{b_B}{2}(T_0^2 - T^2)\right]$$

Substitution into the energy balance then gives

$$\frac{dT}{dt} = \frac{F_0 C_{B0}\left[a_B(T_0 - T) + \frac{b_B}{2}(T_0^2 - T^2)\right] + V r_Q}{V\rho c_p}$$

## 1.2.6
## Momentum Balances

Momentum balance equations are of importance in problems involving the flow of fluids. Momentum is defined as the product of mass and velocity and as stated by Newton's second law of motion, force which is defined as mass times acceleration is also equal to the rate of change of momentum. The general balance equation for momentum transfer is expressed by

$$
\begin{pmatrix}
\text{Rate of change} \\
\text{of momentum} \\
\text{with respect to} \\
\text{time}
\end{pmatrix}
=
\begin{pmatrix}
\text{Rate of} \\
\text{momentum} \\
\text{into the} \\
\text{system}
\end{pmatrix}
-
\begin{pmatrix}
\text{Rate of} \\
\text{momentum} \\
\text{out of the} \\
\text{system}
\end{pmatrix}
+
\begin{pmatrix}
\text{Rate of} \\
\text{generation} \\
\text{of} \\
\text{momentum}
\end{pmatrix}
$$

Force and velocity are however both vector quantities and in applying the momentum balance equation, the balance should strictly sum all the effects in three dimensional space. This however is outside the scope of this text, and the reader is referred to more standard works in fluid dynamics.

As for the mass and energy balance equations, steady-state conditions are obtained when the rate of change of momentum in the system is zero and

$$
\begin{pmatrix}
\text{Rate of} \\
\text{momentum} \\
\text{into the} \\
\text{system}
\end{pmatrix}
-
\begin{pmatrix}
\text{Rate of} \\
\text{momentum} \\
\text{out of the} \\
\text{system}
\end{pmatrix}
+
\begin{pmatrix}
\text{Rate of} \\
\text{generation} \\
\text{of} \\
\text{momentum}
\end{pmatrix}
= 0
$$

Three forms of force, important in chemical engineering flow problems, are pressure forces, shear or viscous forces and gravitational forces (Froment and Bischoff, 1990).

The pressure force is given as the product of pressure and applied area. They are usually taken to be positive when acting on the system surroundings. Shear or viscous forces are also usually taken to be positive when acting on the surroundings and shear force is again the product of shear stress and the applied area. The gravitational forces consist of the force exerted by gravity on the fluid and is equal to the product of the mass of fluid in the control volume times the local acceleration due to gravity. The simulation example TANKHYD utilizes a simple momentum balance to calculate flow rates.

## 1.2.7
## Dimensionless Model Equations

The model mass and energy balance equations will have consistent units, throughout, i.e., kg/s, kmol/s or kJ/s, and corresponding dimensions of mass/time or energy/time. The major system variables, normally concentration or

temperature, will also be expressed in terms of particular units, e.g., kmol/m$^3$ or °C, and the model solution will also usually be expressed in terms of the resultant concentration or temperature profiles, obtained with respect to either time or distance. Each variable will have some maximum value, which is usually possible to establish by simple inspection of the system. Time, as a variable, usually does not have a maximum value, but some characteristic value of time can always be identified. Using these values, a new set of dimensionless variables can be obtained, simply, by dividing all the variables by the appropriate maximum value or by the characteristic time value. This leads to a model composed of dependent variables that vary only between the limits of zero and unity. This means that the solution may, for example, be in terms of the variation of dimensionless concentration versus dimensionless time, and now has a much greater significance, since the particular units of the problem are no longer relevant to the model formulation. The model can now be used much more generally. Furthermore, the various parameters in the original model can be grouped together such that each group of terms also becomes dimensionless. As an added result, the model equations can now be formulated in terms of a fewer number of dimensionless groups than the original number of single parameters. In addition to extending the utility of the mathematical models, the resulting dimensionless groups are especially valuable in correlating experimental data. The above procedure is best illustrated in the simulation examples (BATCHD, TANKD, HOMPOLY, KLADYN, TUBED, TUBDYN, DISRE, DISRET, ENZSPLIT, ENZDYN and BEAD).

### 1.2.7.1  Case A: Continuous Stirred-Tank Reactor (CSTR)

The material balance for a continuous-flow, stirred-tank reactor with constant volume and first-order reaction is

$$V\frac{dC_{A1}}{dt} = (F_0 C_{A0}) - (F_1 C_{A1}) + k_1 C_{A1} V$$

and this is treated in more detail in Chapter 3. The dimensions for each term in the above equation are those of mass per unit time and the units would normally be kmol/s or kg/s.

Dividing the balance equation by the volume of reactor, V, leads to the equation in the form

$$\frac{dC_{A1}}{dt} = \frac{C_{A0} - C_{A1}}{\tau} - kC_{A1}$$

This equation has two parameters $\tau$, the mean residence time ($\tau = V/F$) with dimensions of time and k, the reaction rate constant with dimensions of reciprocal time, applying for a first-order reaction. The concentration of reactant A in the reactor cannot, under normal circumstances, exceed the inlet feed value, $C_{A0}$, and thus a new dimensionless concentration, $\bar{C}_{A1}$, can be defined as

$$\bar{C}_{A1} = \frac{C_{A1}}{C_{A0}}$$

such that $\bar{C}_{A1}$ normally varies in the range from zero to one.

The other variable time, t, can vary from zero to some undetermined value, but the system is also represented by the characteristic time, $\tau$. Note that the value of 1/k also represents a characteristic time for the process.

A new dimensionless time variable is defined here as

$$t = \tau \bar{t}$$

Alternatively the dimensionless time variable

$$\bar{t} = kt$$

could be employed.

In terms of the dimensionless variables, the original variables are

$$C_{A1} = C_{A0}\bar{C}_{A1}$$
$$dC_{A1} = C_{A0}d\bar{C}_{A1}$$
$$t = \tau$$
$$dt = \tau d\bar{t}$$

When substituted into the model equation, the result is

$$\frac{C_{A0}}{\tau}\frac{d\bar{C}_{A1}}{d\bar{t}} = \frac{C_{A0} - C_{A0}\bar{C}_{A1}}{\tau} - kC_{A0}\bar{C}_{A1}$$

This equation can now be rearranged such that the parameter for the time derivative is unity. Thus dividing by $C_{A0}$ and multiplying by $\tau$ gives

$$\frac{d\bar{C}_{A1}}{d\bar{t}} = 1 - \bar{C}_{A1} - (k\tau)\bar{C}_{A1}$$

The parameter term $(k\tau)$, which is called the Damköhler Number Da, is dimensionless and is now the single governing parameter in the model. This results in a considerable model simplification because originally the three parameters, $\tau$, k and $C_{A0}$, all appeared in the model equation.

The significance of this dimensionless equation form is now that only the parameter $(k\tau)$ is important; and this alone determines the system dynamics and the resultant steady state. Thus, experiments to prove the validity of the model need only consider different values of the combined parameter $(k\tau)$.

For this, the dimensionless reactant concentration, $\bar{C}_{A1}$, should be plotted versus dimensionless time, $\bar{t}$, for various values of the dimensionless system parameter $(k\tau)$. Although, k is not an operating variable and cannot be set inde-

pendently, this type of plot may be useful estimating a value from experimental data, as illustrated below.

At steady state

$$0 = 1 - \bar{C}_{A1} - (k\tau)\bar{C}_{A1}$$

so that

$$(k\tau) = \frac{1 - \bar{C}_{A1}}{\bar{C}_{A1}}$$

Knowing $\tau$ thus permits determination of the value k from experimental data.

Consider an nth-order reaction, the equivalent dimensionless model for the stirred-tank reactor becomes

$$\frac{d\bar{C}_{A1}}{d\bar{t}} = 1 - \bar{C}_{A1} - \left(k\tau C_{A0}^{n-1}\right)\bar{C}_{A1}^{n}$$

The variables are defined as previously. Thus if, for example, experimental data is to be tested for second-order reaction behaviour, then data plotted as $\bar{C}_{A1}$ versus $\bar{t}$ should be examined from experiments, for which $(k\tau C_{A0})$ is kept constant.

### 1.2.7.2 Case B: Gas-Liquid Mass Transfer to a Continuous Tank Reactor with Chemical Reaction

A second-order reaction takes place in a two-phase continuous system. Reactant A is supplied by gas-liquid transfer, and reactant B is supplied by liquid feed as depicted in Fig. 1.20.

The model equations are

$$V\frac{dC_{A1}}{dt} = K_L a(C_A^* - C_{A1})V - kC_{A1}C_{B1}V - FC_{A1}$$

$$V\frac{dC_{B1}}{dt} = FC_{B0} - FC_{B1} - kC_{A1}C_{B1}V$$
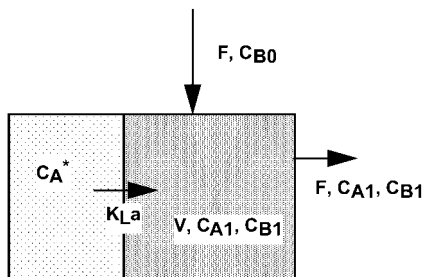


**Fig. 1.20** Two phase continuous reactor with supply of reactant A from gas phase.

The gas-liquid saturation value, $C_A^*$, will be assumed constant.

Dimensionless variables can be defined as

$$\bar{C}_{A1} = \frac{C_{A1}}{C_{B0}}$$

$$\bar{C}_{B1} = \frac{C_{B1}}{C_{B0}}$$

$$\bar{t} = K_L a t$$

The equations become

$$\frac{d\bar{C}_{A1}}{d\bar{t}} = \left(\frac{C_A^*}{C_{B0}} - \bar{C}_{A1}\right) - \frac{kC_{B0}}{K_L a}\bar{C}_{A1}\bar{C}_{B1} - \frac{1}{K_L a \tau}\bar{C}_{A1}$$

$$\frac{d\bar{C}_{B1}}{d\bar{t}} = \frac{1}{K_L a \tau}(1 - \bar{C}_{B1}) - \frac{kC_{B0}}{K_L a}\bar{C}_{A1}\bar{C}_{B1}$$

where $\tau$ is the residence time (= V/F). The number of parameters is reduced, and the equations are in dimensionless form.

An equivalency can be demonstrated between the concept of time constant ratios and the new dimensionless parameters as they appear in the model equations. The concept of time constants is discussed in Section 2.2.

Thus the variables in this example can be interpreted as follows

$$\frac{1}{K_L a \tau} = \frac{\text{Transfer time constant}}{\text{Residence time constant}} = \frac{\text{Convection rate}}{\text{Transfer rate}}$$

and

$$\frac{kC_{B0}}{K_L a} = \frac{\text{Transfer time constant}}{\text{Reaction time constant}} = \frac{\text{Reaction rate}}{\text{Transfer rate}}$$

Further examples of the use of dimensionless terms in dynamic modelling applications are given in Sections 1.2.5.1, 4.3.6.1 and 4.3.7 and in the simulation examples KLADYN, DISRET, DISRE, TANKD and TUBED.

## 1.3
## Chemical Kinetics

### 1.3.1
### Rate of Chemical Reaction

By simplifying the general component balance of Section 1.2.4, the material balance for a batch reactor becomes

$$\begin{pmatrix} \text{Rate of} \\ \text{accumulation} \\ \text{of mass} \\ \text{of component i} \\ \text{in the system} \end{pmatrix} = \begin{pmatrix} \text{Rate of} \\ \text{production of} \\ \text{component i} \\ \text{by reaction} \end{pmatrix}$$

Expressed in terms of volume V and concentration $C_i$, this is equivalent to

$$\frac{d(VC_i)}{dt} = r_i V$$

with units of moles/time. Here the term $r_i$ is the rate of chemical reaction, expressed as the change in the number of moles of a given reactant or product per unit time and per unit volume of the reaction system. Thus for a batch reactor, the rate of reaction for reactant i can be defined as

$$r_i = \frac{1}{V}\frac{dn_i}{dt} \qquad \frac{\text{moles of i}}{\text{volume time}}$$

where $n_i = VC_i$ and it is the number of moles of i present at time t. Alternatively the rate equation may be expressed in terms of mass, kg.

The reactants and products are usually related by a stoichiometric equation which is usually expressed as a molar relationship. For the case of components A and B reacting to form product C it has the form

$$v_A A + v_B B \rightarrow v_C C$$
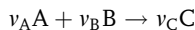
$v_i$ is the stoichiometric coefficient for species i in the reaction. By convention, the value of $v$ is positive for the products and negative for the reactants. The stoichiometric coefficients relate the simplest ratio of the number of moles of reactant and product species, involved in the reaction.

The individual rates of reaction, for all the differing species of a reaction, are related via their stoichiometric coefficients according to

$$r_i = r_j \left( \frac{v_i}{v_j} \right)$$

The value of $r_i$ is therefore negative for reactants and positive for products.

For the reaction

$$A + 2B \rightarrow 3P$$
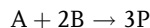
the individual reaction rates are therefore

$$-r_A = -\frac{1}{2}r_B = \frac{1}{3}r_P$$

Thus in defining the rate of reaction, it is important to state the particular species.

The temperature and concentration dependencies of reaction rates can usually be expressed as separate functions, for example

$$r_A = k_0 f_1(T) f_2(C_A)$$

The dependency of temperature $f_1(T)$ is usually described as the Arrhenius Equation, as explained in the next section.

The exact functional dependence of the reaction rate with respect to concentration must be found by experiment, and for example may have the general form

$$r_A = -k C_A^{\alpha} C_B^{\beta}$$

Here k is the reaction rate constant, which is a function of temperature only; $C_A$, $C_B$ are the concentrations of the reactants A, B (moles/volume); $\alpha$ is the order of reaction, with respect to A; $\beta$ is the order of reaction, with respect to B; $(\alpha + \beta)$ is the overall order of the reaction. Whatever reference quantity is used to define specific rates this needs to be stated clearly.

It is important to realize that the reaction rate may represent the overall summation of the effect of many individual elementary reactions, and therefore only rarely represents a particular molecular mechanism. The orders of reaction, $\alpha$ or $\beta$, can not be assumed from the stoichiometric equation and must be determined experimentally.

For heterogeneous catalytic reactions, the rate of reaction is often expressed as the number of moles (or kg) of component reacting per unit time, per unit mass of catalyst. For a batch reactor

$$r_A = \frac{1}{M} \frac{dn_A}{dt} \qquad \frac{\text{moles}}{\text{mass time}}$$

where M is the mass of catalyst. Sometimes the surface area is used as the reference quantity for solid surface reactions.

In vapour phase reactions, partial pressure units are often used in place of concentration in the rate equation, for example

$$r_A = -k p_A^{\alpha} p_B^{\beta}$$

where $p_A$ and $p_B$ are the gas phase partial pressures of reactants A and B. In this case, k would be expressed in terms of pressure units. Detailed treatments of chemical kinetics are found e.g. in Walas (1989), Missen et al. (1999), Levenspiel (1999).

## 1.3.2
### Reaction Rate Constant

The reaction constant, k, is normally an exponential function of the absolute temperature, T, and is described by the Arrhenius equation

$$k = Ze^{-E/RT}$$

The exponential term gives rise to the highly non-linear behaviour in reactor systems which are subject to temperature changes.

The parameters Z and E, the activation energy, are usually determined by measuring k, over a range of temperatures, and plotting ln k versus the reciprocal absolute temperature, 1/T, as shown in Fig. 1.21.

High reaction temperatures can cause numerical overflow problems in the computer calculation of k, owing to the very large values generated by the exponential term. This can often be eliminated by defining a value of the rate constant, $k_0$, for some given temperature, $T_0$.

Thus

$$k_0 = Ze^{-E/RT_0}$$

The logarithmic form of the Arrhenius relationship is then

$$\ln \frac{k}{k_0} = -\frac{E}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right)$$

which permits the calculation of k at any temperature T. The above procedure is used in the simulation examples THERM and THERMPLOT.
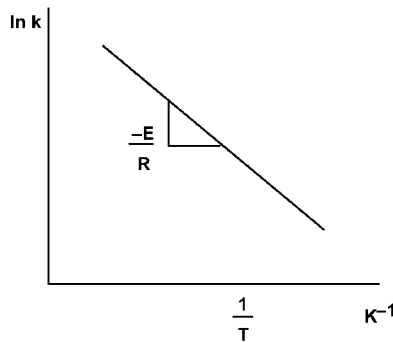


**Fig. 1.21** Arrhenius plot for determining activation energy.

1.3.3
**Heat of Reaction**

The heat of reaction, $\Delta H$, can be calculated from the heats of formation or heats of combustion

$$\Delta H = \sum_{i=1}^{n} v_i \Delta H_{Fi} = \sum_{i=1}^{n} v_i \Delta H_{Ci}$$

where $\Delta H_{Fi}$ is the heat of formation of component i, $\Delta H_{Ci}$ is the heat of combustion of component i and $v_i$ is the stoichiometric coefficient for component i. If heats of formation are not available, heats of combustion can easily be determined from calorimetric heats of combustion data. The resulting heat of reaction, $\Delta H$, can be calculated and by convention is negative for exothermic reactions and positive for endothermic reactions. The temperature dependence of $\Delta H$ is described in Section 1.2.5. For complex reaction systems, the heats of reaction of all individual reactions have to be estimated, and the dynamic heat balance equations must include the heats of all the reactions.

1.3.4
**Chemical Equilibrium and Temperature**

Chemical equilibrium depends on temperature as described by the van't Hoff equation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

Here K is the thermodynamic chemical equilibrium constant. If $\Delta H$ is constant, direct integration yields an explicit expression. If $\Delta H$ is a function of temperature, as described in Section 1.3.3, then its dependency on $c_p$ can be easily included and integration is again straight-forward. A calculation with varying $\Delta H$ and $c_p$ as functions of temperature is given in the simulation example REVTEMP developed in Section 1.2.5.3.

1.3.5
**Yield, Conversion and Selectivity**

The fractional conversion of a given reactant, $X_A$, is defined for a batch system as

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A initially present}}$$

giving

$$X_A = \frac{n_{A0} - n_A}{n_{A0}}$$

or

$$n_A = n_{A0}(1 - X_A)$$

and at constant volume

$$X_A = \frac{C_{A0} - C_A}{C_{A0}}$$

where $n_{A0}$ is the initial number of moles of A, $n_A$ is the number of moles of A at fractional conversion $X_A$ and $(n_{A0}-n_A)$ is the number of moles of A reacted. From this it follows for a constant-volume batch system that

$$r_A = -\frac{n_{A0}}{V}\frac{dX_A}{dt}$$

For a well-mixed flow system at steady state, the fractional conversion $X_A$ is the ratio of the number of moles of A converted to the moles A fed to the system

$$X_A = \frac{F_0 C_{A0} - F_1 C_{A1}}{F_0 C_{A0}}$$

where for equal volumetric flow rates at inlet and outlet $(F_0 = F_1)$

$$X_A = \frac{C_{A0} - C_{A1}}{C_{A0}}$$

This definition is identical to that of the batch case.

Fractional yield is defined by

$$Y_{C/A} = \frac{\text{Moles of A transformed into a given product C}}{\text{Total moles of A reacted}}$$

Again it is important that both the particular reactant and product, concerned, should be stated, when defining a fractional yield.

A definition of instantaneous fractional yield is based on the ratio of reaction rates

$$Y_{C/A} = \frac{r_C}{-r_A}$$

where A is the key reactant and C the product.

Multiple reaction selectivity can be defined similarly as the ratio of the rate of formation of the desired product to the formation rate of an undesired product as in a parallel reaction

$$A \diagup_C^B$$

where

$$S_{B,C} = \frac{r_B}{r_C}$$

Here $S_{B,C}$ is the instantaneous selectivity of the desired product B to unwanted product in this parallel reaction.

## 1.3.6
## Microbial Growth Kinetics

Under ideal batch growth conditions, the quantity of biomass, and therefore the biomass concentration will increase exponentially with respect to time and in accordance with all cells having the same probability to multiply. Thus the overall rate of biomass formation is proportional to the biomass itself where

$$r_X = kX$$

Here $r_X$ is the rate of cell growth (kg cell $m^{-3}$ $s^{-1}$), X is the cell concentration (kg cell $m^{-3}$) and k is a kinetic growth constant ($s^{-1}$). For a batch system, this is equivalent to

$$\frac{dX}{dt} = kX$$

where dX/dt is the rate of change of cell concentration with respect to time (kg cell $m^{-3}s^{-1}$). The analytical solution of this simple first order differential equation is

$$\frac{X}{X_0} = e^{kt}$$

where $X_0$ is the initial cell concentration at time t=0.

The plot of the logarithm of cell concentration versus time will often yield a straight line over a large portion of the curve, as shown in Fig. 1.22.

   The initial time period up to $t_1$ represents a period of zero growth, which is known as the lag phase. In this period the cells synthesise enzymes and other cellular components appropriate to the particular environmental conditions of the fermentation.

   An exponential (or logarithmic) growth phase follows the lag phase, and during this period the cell mass increases exponentially. The growth rate is at a maximum during this phase, and the population of cells are fairly uniform with respect to chemical composition and metabolic composition.
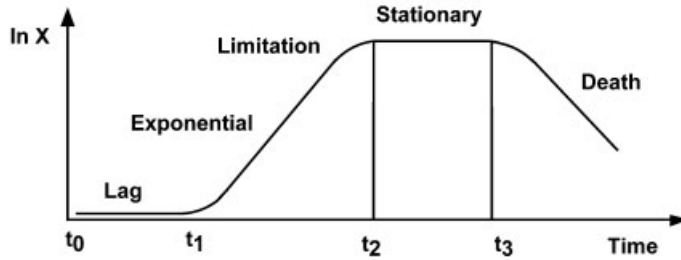
**Fig. 1.22** Biomass concentration during batch growth.

The growth of micro-organisms in a batch reactor will eventually end, owing either to the depletion of some essential nutrient or perhaps to the accumulation of some toxic product. The result is that the growth rate gradually slows, and the growth becomes nutrient limited or product inhibited. When the growth rate falls to that of the cell death rate, the cell concentration remains constant, during the stationary phase part of the curve.

Following the stationary phase the rate of cell death exceeds that of cell growth, and the cell number begins to decrease, resulting in the final death rate part of the curve.

The slope of the curve in the limitation region decreases as it approaches $t_2$. The slope represents the growth rate per unit mass of cells or specific growth rate and is given the symbol $\mu$ (s$^{-1}$), where:

$$\frac{d \ln X}{dt} = \frac{1}{X}\frac{dX}{dt} = \text{specific growth rate} = \mu$$

In many processes, cells may die continuously or may start dying (after time, $t_3$) because of a lack of nutrients, toxic effects or cell ageing. This process can typically be described by a first order decay relationship:

$$r_d = -k_d X$$

where $r_d$ is the death rate and $k_d$ (s$^{-1}$) is the specific death rate coefficient.

The exponential and limiting regions of cell growth can be described by a single relation, in which $\mu$ is a function of substrate concentration, i.e., the Monod equation

$$\mu = \frac{\mu_{max}S}{K_S + S}$$

Although very simple, the Monod equation frequently describes experimental growth rate data very well. The form of this relation is shown in Fig. 1.23.
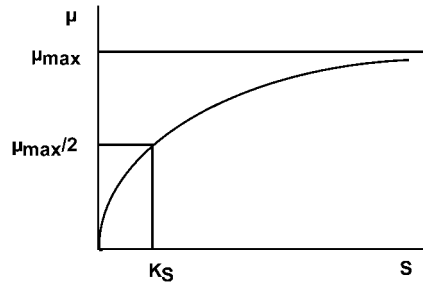
**Fig. 1.23** Specific growth rate versus limiting substrate concentration according to the Monod relation.

The important properties of this relationship are as follows:

$$S \to 0 \, , \quad \mu \to \frac{\mu_{max}}{K_S} S$$

$$S \to \infty \, , \quad \mu \to \mu_{max}$$

$$S = K_S \, , \quad \mu = \frac{\mu_{max}}{2}$$

**Substrate Uptake Kinetics**

The rate of uptake of substrate by micro-organisms is generally considered to be related to the rate of growth and to the rate required for maintenance,

$$r_S = \frac{-r_X}{Y_{X/S}} - mX$$

Here $r_S$ is the rate of substrate uptake by the cells (kg substrate m$^{-3}$ s$^{-1}$). $Y_{X/S}$ (kg/kg) is the stoichiometric factor or yield coefficient, relating the mass of cell produced per unit mass of substrate consumed and the maintenance factor m (kg substrate/kg biomass S), represents the utilisation of substrate by the cells for non-growth related functions.

For further details of microbial kinetics refer to Dunn et al. (2003), Moser (1988), Shuler and Kargi (1999) and Blanch and Clark (1996).

**1.4**
**Mass Transfer Theory**

1.4.1
**Stagewise and Differential Mass Transfer Contacting**

Mass transfer separation processes, e.g., distillation, gas absorption, etc., are normally treated in terms of stagewise or differential procedures. In a stagewise procedure, concentration changes are taken to occur in distinct jumps, as, for
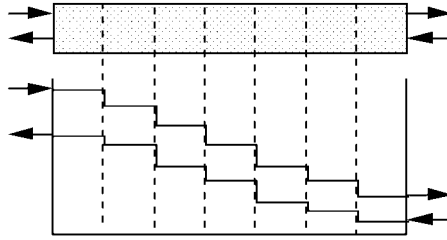
**Fig. 1.24** Concentration profiles for countercurrent, stagewise contactor.

example, between the neighbouring plates of a distillation column. In a differential procedure the concentrations are assumed to vary continuously throughout the total length or volume of the contactor, as, in say, a packed bed gas absorption column. The two different types of operation lead to two quite distinct design approaches, namely a stagewise design and a differential design. Both can be handled to advantage by simulation methods.

Figure 1.24 shows a countercurrent stagewise mass transfer cascade and the resulting staged profile of the two streams, owing to the mass transfer between the streams.

In the stagewise simulation method the procedure is based on the assessment of the separation achieved by a given number of equilibrium contacting stages. The concept of the equilibrium stage is illustrated, for a particular stage n of the cascade, as shown in Fig. 1.25.
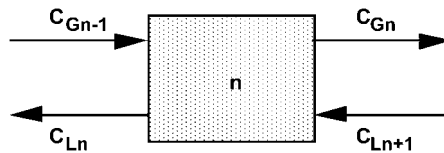


**Fig. 1.25** Equilibrium mass-transfer stage.

According to this assumption the two streams are so well mixed that the compositions of each phase within the stage are uniform. Further, the mass transfer is so efficient that the compositions of the streams leaving the stage are in equilibrium.

$$C_{Ln} = f_{eq}(C_{Gn})$$

The actual stage can be a mixing vessel, as in a mixer-settler used for solvent extraction applications, or a plate of a distillation or gas absorption column. In order to allow for non-ideal conditions in which the compositions of the two exit streams do not achieve full equilibrium, an actual number of stages can be related to the number of theoretical stages, via the use of a stage-efficiency factor. Also it will be seen that a rate approach will account for this.
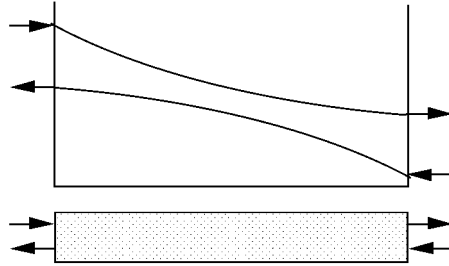
**Fig. 1.26** Concentration profiles for countercurrent, differential contactor.

Figure 1.26 shows a differential type of contactor as in, say, a countercurrent flow-packed gas absorption column, together with the resulting approximate continuous concentration profiles.

In this type of apparatus, the two phases do not come to equilibrium, at any point in the contactor and the simulation method is based, therefore, not on a number of equilibrium stages, but rather on a consideration of the relative rates of transport of material through the contactor by flow and the rate of interfacial mass transfer between the phases. For this, a consideration of mass transfer rate theory becomes necessary.

### 1.4.2
### Phase Equilibria

Knowledge of the phase equilibrium is essential for any mass transfer process, since this is, by definition, implicit in the idea of a theoretical stage. It is also important, however, in determining the concentration driving-force term in the mass-transfer rate expression. At phase equilibrium conditions, the driving force for mass transfer is zero and therefore further concentration changes via a mass transfer mechanism become impossible. The equilibrium is therefore also important in determining the maximum extent of the concentration change, possible by mass transfer.

Equilibrium data correlations can be extremely complex, especially when related to non-ideal multicomponent mixtures, and in order to handle such real life complex simulations, a commercial dynamic simulator with access to a physical property data-base often becomes essential. The approach in this text is based, however, on the basic concepts of ideal behaviour, as expressed by Henry's Law for gas absorption, the use of constant relative volatility values for distillation and constant distribution coefficients for solvent extraction. These have the advantage that they normally enable an explicit method of solution and avoid the more cumbersome iterative types of procedure, which would otherwise be required. Simulation examples in which more complex forms of equilibria are employed are STEAM and BUBBLE.
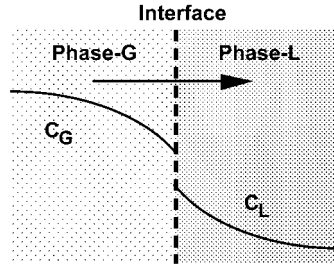
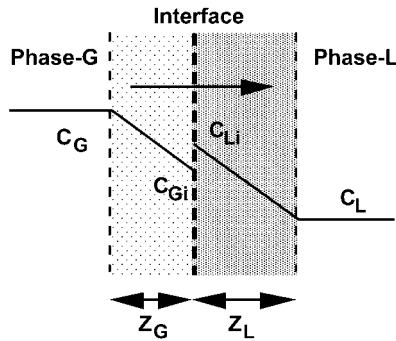**Fig. 1.27** Concentration gradients at a gas-liquid interface.



**Fig. 1.28** Concentration gradients according to the Whitman Two-Film theory.

### 1.4.3
### Interphase Mass Transfer

Actual concentration profiles (Fig. 1.27) in the very near vicinity of a mass transfer interface are complex, since they result from an interaction between the mass transfer process and the local hydrodynamic conditions, which change gradually from stagnant flow, close to the interface, to more turbulent flow within the bulk phases.

According to the Whitman Two-Film theory, the actual concentration profiles, as shown in Fig. 1.27, are approximated for the steady state with no chemical reaction, by that of Fig. 1.28.

The above theory makes the following assumptions:
1. A thin film of fluid exists on either side of the interface.
2. Each film is in stagnant or laminar flow, such that mass transfer across the films is by a process of molecular diffusion and can therefore be described by Fick's Law.
3. There is zero resistance to mass transfer at the interface, itself, and therefore the concentrations at the interface are in local equilibrium.

4. Each of the bulk phases, outside the films, are in turbulent flow. Concentrations within the bulk phases are therefore uniform and the bulk phases constitute zero resistance to mass transfer.
5. All the resistance to mass transfer therefore occurs within the films.

Fick's Law states that the flux j (mol/s m$^2$) for molecular diffusion, for any given component is given by

$$j = -D\frac{dC}{dZ}$$

where D is the molecular diffusion coefficient (m$^2$/s), and dC/dZ is the steady-state concentration gradient (mol/m$^3$m). Thus applying this concept to mass transfer across the two films

$$j_A = D_G\frac{C_G - C_{Gi}}{Z_G} = D_L\frac{C_{Li} - C_L}{Z_L}$$

where $D_G$ and $D_L$ are the effective diffusivities of each film, and $Z_G$ and $Z_L$ are the respective thicknesses of the two films.

The above equations can be expressed as

$$j = k_G(C_G - C_{Gi}) = k_L(C_{Li} - C_L)$$

where $k_G$ and $k_L$ (m/s) are the mass transfer coefficients for the G-phase and L-phase films, respectively.

The total rate of mass transfer, Q (mol/s), is given by

$$Q = jA = j(aV)$$

where A is the total interfacial area for mass transfer; a is defined as the specific area for mass transfer or interfacial area per volume (m$^2$/m$^3$) and V is the volume (m$^3$).

Thus

$$Q = k_GA(C_G - C_{Gi}) = k_LA(C_{Li} - C_L)$$

or in terms of a and V

$$Q = k_Ga(C_G - C_{Gi})V = k_La(C_{Li} - C_L)V$$

Since the mass transfer coefficient, k, and the specific interfacial area, a, vary in a similar manner, dependent upon the hydrodynamic conditions and system physical properties, they are frequently combined and referred to as a "ka" value or more properly as a mass transfer capacity coefficient.
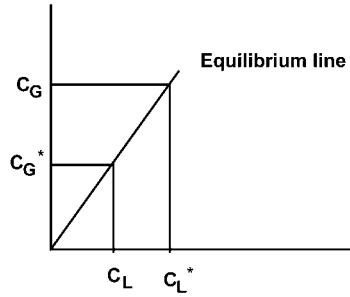
**Fig. 1.29** The bulk phase concentrations determine the equilibrium concentrations.

In the above theory, the interfacial concentrations $C_{Gi}$ and $C_{Li}$ are not measurable directly and are therefore of relatively little immediate use. In order to overcome this apparent difficulty, overall mass transfer rate equations are defined by analogy to the film equations. These are based on overall coefficients of mass transfer, $K_G$ and $K_L$, and overall concentration driving forces, where

$$Q = K_G A \left( C_G - C_G^* \right) = K_L A \left( C_L^* - C_L \right)$$

and $C_G^*$ and $C_L^*$ are the respective equilibrium concentrations, corresponding to the bulk phase concentrations, $C_L$ and $C_G$, respectively, as shown in Fig. 1.29.

Simple algebra, based on a combination of the film and overall mass transfer rate equations, lead to the following equations, relating the respective overall mass transfer coefficients and the coefficients for the two films

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{m}{k_L}$$

and

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{mk_G}$$

where m is the local slope of the equilibrium line

$$m = \frac{dC_G}{dC_L^*}$$

For a non-linear equilibrium relationship, in which the slope of the equilibrium curve varies with concentration, the magnitudes of the overall mass transfer coefficients will also vary with concentration, even when the film coefficients themselves remain constant. The use of overall mass transfer coefficients in mass transfer rate equations should therefore be limited to the case of linear equilibrium or to situations in which the mass transfer coefficient is known to

be relatively insensitive to concentration changes. Design equations based on the use of film mass transfer coefficients and film concentration driving forces make use of the identity that:

$$k_G(C_G - C_{Gi}) = k_L(C_{Li} - C_L)$$

and that the interfacial concentrations $C_{Gi}$ and $C_{Li}$ are in local equilibrium. Examples with mass transfer are OXIDAT, KLADYN and all examples in Section 5.8.